Benchtop GC-ECNI-IDMS Analysis of PBDEs in Fish from Remote Mountain Lakes: Effects of Ion Source Parameters and Br Substitution Patterns
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Benchtop GC-ECNI-IDMS Analysis of PBDEs in Fish from Remote Mountain Lakes: Effects of Ion Source Parameters and Br Substitution Patterns

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Introduction

Polybrominated diphenylether (PBDE) flame-retardants are emerging pollutants with demonstrated atmospheric transport and have been classified as persistent, bioaccumulative, and toxic. PBDE's rising and wide ranging concentrations in environmental matricies are as mixtures of congeners (di-deca BDEs). Naturally occurring and anthropogenic brominated compounds can cause misquantitation of PBDEs in environmental matrices because benchtop GC-ECNI-MS methods often monitor non-specific bromide ions. Specific, high mass, molecular and fragment ions are rarely used for quantitation because of low mass spectral abundances. Optimizing GC-ECNI-IDMS PBDE analysis was complicated by different congeners spanning a large range of physical-chemical properties and MS response. We used GC-ECNI-IDMS (with 13C surrogates) to measure PBDEs in fish. We characterized source parameters' and substitution patterns' effects on these analyses.

Methods

Homogenates of fish from remote mountain lakes were spiked with nine 13C PBDE recovery surrogates, dried with Na2SO4, and extracted with dichloromethane using pressurized liquid extraction. Interferants were removed from the extracts using silica gel and size exclusion chromatography. Final extracts (300uL) were spiked with 13C PCB internal standards and analyzed with an Agilent 6890/5973 GC-ECNI-MS. GC-MS oven and selected ion monitoring programs were developed for analysis of 46 PBDE and 43 SOC targets and surrogates in a single analysis. Specific, high mass molecular and fragment ions (M-xH-yBr) were used for PBDE quantitation. Different congener's bromine substitution patterns were compared to their sensitivity, and variability in the fish PBDE dataset, as well as their different responses to source parameters' optimizations.

Preliminary Results

Our previous work showed PBDE specific high mass molecular and fragment ions (M-xH-yBr) were sensitive to, and had a highly variable response to, changes in ion source parameters. These ions were most affected by, electron energy, system pressure, source temperature, and emission current, respectively. Our work allowed for PBDE quantitation with 13C PBDE surrogates. The sensitivity of our method was not significantly different from previous bromide ion monitoring methods, but the specificity and precision increased with use of 13C PBDE standards.

PBDE congeners' sensitivity and variability was compared to bromine substitution patterns. The number of bromines total, ortho substituted, ortho substituted on opposite rings, and alternately substituted were all positively correlated with PBDE instrumental sensitivity ($p<0.05$ – $p<0.001$, $r = 0.57 – 0.68$). The number of bromines total, ortho substituted on opposite rings, and, most strongly, the number in adjacent pairings were all positively correlated with MS response variability ($p<0.05$ – $p<0.001$, $r = 0.1 – 0.74$). Only the number of alternating bromine pairs was negatively correlated with variability ($p<0.001$, $r = 0.3$). Fish method sensitivity (as measured with method detection limits) and variability (as measured with and calibration checks) showed the same correlations with substitution patterns.

Method detection limits ranged from 0.5 - 2000 pg/g ww (ppt). Method recoveries averaged 72% and ranged from 35 - 95%. Individual PBDE concentrations in fish varied from 2.9 - 4100 pg/g ww. The most prevalent and concentrated PBDEs were #47, #99, #100, and #154 respectively, with PBDE #47 and #99 dominating the profile. These patterns closely match other reports of PBDE congener patterns in fish, although the concentrations measured here extend far below those measured elsewhere.

Results indicate PBDEs are volatile and persistent enough to be transported to, and accumulate within, remote mountain lake ecosystems.

Novel Aspect

The effects of ion source parameters and bromine substitution patterns on the GC-ECNI-IDMS measurement of PBDEs in fish are explored.